

The electrostatic potential of a periodic lattice

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Abstract

We calculate the electrostatic potential of a periodic lattice of arbitrary extended charges by using the Cartesian multipole formalism. This method allows the separation of the long-range potential from the contact potential (potential on the source). We write both the electrostatic potential and the interaction energy as convergent sums in the reciprocal space.

1 Introduction

The calculation of the electrostatic potential of a periodic lattice is an essential step in the study of crystals. For finding the electron energy bands, the Schrodinger and Poisson equations must be solved self-consistently. This subject has been extensively studied in the literature, by different methods (see Ref.[1] and references therein). In this paper we are concerned with the problem of finding the electrostatic potential when the periodic charge distribution is known and we are going to use the multipolar formalism, as presented in Refs. [2], [3], in order to solve this problem. Unlike the Fourier technique, our method has the advantage of separating the quantities which are responsible for the contact interaction and which give us information about the shape and spatial extension of the sources (mean radii) from those which are responsible for the long-range interaction (charge moments). Thus, we are able to correctly separate the overlapping electrostatic energy from the long-range electrostatic energy and to write both of them as convergent series in the reciprocal space.

Our method can be used either together with an ab-initio model of the charge density or in the formalism of pseudo-atom model. We suppose below that we have decided on the form of the charge density attached to a simple Bravais lattice and present the method of calculation of the electrostatic potential and energy. We are considering a simple Bravais lattice for simplifying the formulas, but the formalism can be easily extended to an arbitrary periodic lattice.

The paper is organized as follows: in the next section we present the general mathematical formalism which can be used for a Bravais lattice with extended arbitrary charges. In Sec.3 we study some particular simple charge distributions, with a particular pedagogical emphasis on the lattice of uniformly charged spheres and the end section is devoted to conclusions.

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2 General mathematical formalism

We have proved in Ref.[3] the following formula for the Cartesian multipole expansion of an arbitrary charge distribution:

$$\rho(\mathbf{r}, t) = \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \frac{(-1)^l (2l+1)!!}{2^n n!! (2n+2l+1)!!} \cdot \overline{r_{i_1 \dots i_l}^{2n}}(t) \Delta^n \partial_{i_1} \dots \partial_{i_l} \delta(\mathbf{r}), \quad (1)$$

where $\rho(\mathbf{r}, t)$ is the charge density and

$$\overline{r_{i_1 \dots i_l}^{2n}}(t) = \frac{(-1)^l}{(2l-1)!!} \int d^3\xi \xi^{2l+2n+1} \rho(\xi, t) \partial_{i_1} \dots \partial_{i_l} \frac{1}{\xi} \quad (2)$$

is the electric mean square radius of order n and multipolarity l . The electric mean square radii of order zero are also called electric moments¹. The multipoles in Eq. (1) are calculated with respect to the origin of the coordinate axis. From the above formulas, one can easily calculate the scalar potential by using the formula:

$$\phi(\mathbf{r}, t) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

After integrating by parts one obtains:

$$\phi(\mathbf{r}, t) = \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \frac{(-1)^l (2l+1)!!}{2^n n!! (2n+2l+1)!!} \cdot \overline{r_{i_1 \dots i_l}^{2n}}(t) \Delta^n \partial_{i_1} \dots \partial_{i_l} \frac{1}{r} \quad (4)$$

We consider now a Bravais lattice and some extended identical charge distributions placed on the lattice points. For atomic crystals, these charge distributions are the neutral atoms and for ionic crystals they are the ions which are neutralized by a uniform background. If the crystal is formed by different species of atoms (ions), we can view it as a superposition of simple Bravais lattices. We denote by \mathbf{R}_k a lattice vector. The charge density distribution of the lattice can be written as:

$$\rho(\mathbf{r}, t) = \sum_{\mathbf{R}_k} \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \frac{(-1)^l (2l+1)!!}{2^n n!! (2n+2l+1)!!} \cdot \overline{r_{i_1 \dots i_l}^{2n}}(t) \Delta^n \partial_{i_1} \dots \partial_{i_l} \delta(\mathbf{r} - \mathbf{R}_k), \quad (5)$$

where we have calculated the multipoles for each charge distribution with respect to the origin \mathbf{R}_k . As the charge distributions are identical, their multipoles are identical and they do not need

¹ The sum from the right-hand side of Eq. (1) begins with the monopole which corresponds to $l = 0$. As the monopole is a scalar, it doesn't need a dummy lower index. So, Eq.(1) must be understood as follows: $\rho(\mathbf{r}, t) = \sum_{n=0}^{\infty} \frac{1}{2^n n! (2n+1)!} \overline{r_0^{2n}} \delta(\mathbf{r}) - \sum_{n=0}^{\infty} \frac{3}{2^n n! (2n+3)!} \overline{r_{i_1}^{2n}} \Delta^n \partial_{i_1} \delta(\mathbf{r}) + \dots$

any lattice index. The total scalar potential at an arbitrary point \mathbf{r} of the lattice is :

$$\phi(\mathbf{r}, t) = \sum_{\mathbf{R}_k} \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \frac{(-1)^l (2l+1)!!}{2^n n! l! (2n+2l+1)!!} \cdot \frac{1}{\overline{r_{i_1 \dots i_l}^{2n}}(t) \Delta^n \partial_{i_1} \dots \partial_{i_l} |\mathbf{r} - \mathbf{R}_k|} \quad (6)$$

We process further this expression by separating the contribution of the moments (long-range potentials) from the contribution of the mean-square radii (contact potentials) and use the relations:

$$\Delta \frac{1}{r} = -4\pi \delta(\vec{r}), \quad \sum_{\mathbf{R}_k} \delta(\mathbf{r} - \mathbf{R}_k) = \frac{1}{\Omega} \sum_{\mathbf{g}} e^{i\mathbf{g}\mathbf{r}}, \quad (7)$$

where Ω is the volume of one elementary cell and \mathbf{g} is a vector in the reciprocal space. One obtains:

$$\begin{aligned} \phi(\mathbf{r}, t) = & \sum_{\mathbf{R}_k} \sum_{l=0}^{\infty} \frac{(-1)^l}{l!} \overline{r_{i_1 \dots i_l}^0}(t) \partial_{i_1} \dots \partial_{i_l} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} - \\ & \frac{4\pi}{\Omega} \sum_{\mathbf{g}} \sum_{l=0}^{\infty} \sum_{n=1}^{\infty} \frac{i^l (-1)^l (2l+1)!! (-1)^{n-1} g^{2n-2}}{2^n n! l! (2l+2n+1)!!} \cdot \\ & \overline{r_{i_1 \dots i_l}^{2n}}(t) g_{i_1} \dots g_{i_l} e^{i\mathbf{g}\mathbf{r}}. \end{aligned} \quad (8)$$

Now, using $W(t) = \int d\mathbf{r} \rho(\mathbf{r}, t) \phi(\mathbf{r}, t)$, after integrating by parts, we obtain the energy of the charge distribution placed at $\mathbf{r} = \mathbf{R}_0$ in the potential $\phi(\mathbf{r}, t)$:

$$\begin{aligned} W(t) = & \sum_{l=0}^{\infty} \frac{1}{l!} \overline{r_{i_1 \dots i_l}^0}(t) (\partial_{i_1} \dots \partial_{i_l} \phi(\mathbf{r}, t))_{\mathbf{r}=\mathbf{R}_0} \\ & + \sum_{l=0}^{\infty} \sum_{n=1}^{\infty} \frac{(2l+1)!!}{2^n n! l! (2l+2n+1)!!} \cdot \\ & \overline{r_{i_1 \dots i_l}^{2n}}(t) (\Delta^n \partial_{i_1} \dots \partial_{i_l} \phi(\mathbf{r}, t))_{\mathbf{r}=\mathbf{R}_0}. \end{aligned}$$

The first term of r.h.s. the above formula is the long-range interaction energy, while the second term is different from zero only when $(\Delta \phi(\mathbf{r}))_{\mathbf{r}=\mathbf{R}_0} \neq 0$, that is, when there exist non-zero overlap between the charge at $\mathbf{r} = \mathbf{R}_0$ and some of the other charges (contact or overlapping energy, including the self-energy). The formulas of this section are valid for an arbitrary time-dependence, but in the following we shall consider only the electrostatic case.

3 Particular charge densities

We apply the general formalism of the previous section for some particular charge distributions. We shall analyse in greater detail the case of a uniformly charged sphere and, for pedagogical purposes, we shall calculate the potential of a uniformly charged sphere in two ways: first by using the spherical multipole expansion of the Green function and then by using the Cartesian multipole expansion of the charge density. Then, we shall shortly present the results for the potential and interaction energy for other interesting charge distributions.

3.1 Constant charge density

3.1.1 The potential of a uniformly charged sphere

In many electrodynamics textbooks we can find the following method for calculating the electrostatic potential of a uniformly charged sphere: from the Poisson equation $\Delta\phi(\mathbf{r}) = -4\pi\rho(\mathbf{r})$ one finds using the Green theorem:

$$\phi(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (9)$$

After inserting in the above equation the expansion:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l,m} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(\theta, \phi) Y_{l,m}^*(\theta', \phi'),$$

using the fact that the charge density is spherically symmetric, one obtains:

$$\phi(\mathbf{r}) = 4\pi \int_0^\infty dr' r'^2 \rho(r') \left[\theta(r - r') \frac{1}{r} + \theta(r' - r) \frac{1}{r'} \right]. \quad (10)$$

Using for the charge density the expression:

$$\rho(\mathbf{r}) = C\theta(a - r), \quad (11)$$

where C is a constant and replacing $\theta(r - r') = 1 - \theta(r' - r)$, after elementary integrations one finds:

$$\phi(\mathbf{r}) = \frac{4\pi a^3 C}{3r} + 4\pi C \left(\frac{a^2}{2} - \frac{a^3}{3r} - \frac{r^2}{6} \right) \theta(a - r). \quad (12)$$

In order to separate the potential inside the sphere from the potential outside it, one uses $1 = \theta(r - a) + \theta(a - r)$ and one finally finds the well known result:

$$\phi(\mathbf{r}) = \frac{4\pi a^3 C}{3r} \theta(r - a) + \frac{2\pi C}{3} (3a^2 - r^2) \theta(a - r). \quad (13)$$

Now, we are going to obtain the same result for the electrostatic potential by using the method of Cartesian multipole expansion. For the charge density (11) one can easily see that the only non-zero multipoles are the charge monopole and its (infinite number of) mean square radii. After a simple calculation one finds the following expression of a charge mean square radius of order n :

$$\overline{r_0^{2n}} = 4\pi C \frac{a^{2n+3}}{2n+3} \quad (14)$$

When we introduce Eqs. (11) and (14) in Eq. (1) we find:

$$\theta(a - r) = 4\pi \sum_{n=0}^{\infty} \frac{a^{2n+3}}{2^n n! (2n+3)!!} \Delta^n \delta(\mathbf{r}). \quad (15)$$

The above formula is a particular case of Eq. (1), which was rigorously justified in Ref. [3]. On the other hand, it can be formally obtained by integrating after "a" the expansion:

$$\delta(a - r) = 4\pi \sum_{k=0}^{\infty} \frac{a^{2k+2}}{2^k k! (2k+1)!!} \Delta^k \delta(\mathbf{r}), \quad (16)$$

which is a particular case of the mean value formula of Pizzetti ([4]). Note that both Eqs. (15), (16) can be justified in the Fourier space. Thus, by taking the Fourier transform $\int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}}$ of Eq. (16) one obtains:

$$\frac{4\pi a}{k} \sin(ka) = 4\pi a \sum_{n=0}^{\infty} \frac{(-1)^n a^{2n+1} k^{2n+1}}{2^n n! (2n+1)!!},$$

which, after using $(2n+1)!! = \frac{(2n+1)!}{2^n n!}$, is exactly the Taylor expansion of the function $\sin(ka)$. If we take the Fourier transform of Eq. (15) we obtain:

$$\frac{4\pi a^2}{k} j_1(ka) = 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n a^{2n+3} k^{2n}}{2^n n! (2n+3)!!},$$

which is exactly the Taylor expansion of the spherical Bessel function $j_1(ka)$. By the same method of Fourier transforms one can justify the formula:

$$\frac{\theta(a-r)}{r} = 4\pi \sum_{n=0}^{\infty} \frac{a^{2n+2}}{2^{n+1} (n+1)! (2n+1)!!} \Delta^n \delta(\mathbf{r}). \quad (17)$$

The series of Dirac delta functions and its derivatives which appear in Eqs. (15), (16), (17) are called in the literature dual Taylor series and their correspondence with the usual Taylor series is rigorously studied in Ref. [5].

We return now to our calculation of the electrostatic potential: inserting Eqs. (11), (15) into Eq. (9) one obtains after integrating by parts:

$$\phi(\mathbf{r}) = \frac{4\pi a^3 C}{3r} - 16\pi^2 C \sum_{k=1}^{\infty} \frac{a^{2k+3}}{2^k k! (2k+3)!!} \Delta^{k-1} \delta(\mathbf{r}). \quad (18)$$

The first term of the above equation is the contribution of the monopole to the electrostatic potential and it is singular at $r = 0$. The second term is the contribution of the mean square radii to the electrostatic potential and it contains a singular contribution at $r = 0$ (which exactly compensates the contribution of the monopole) and a finite contribution which is exactly the potential inside the sphere. Now, we use in Eq. (18) the relation $1 = \theta(r-a) + \theta(r+a)$ and Eq. (17), in order to separate the potential inside the sphere from the potential outside it. We obtain:

$$\phi(\mathbf{r}) = \frac{4\pi a^3 C}{3r} \theta(r-a) + \frac{16\pi^2 C}{3} \sum_{k=0}^{\infty} \frac{a^{2k+5}}{2^k k! (2k+5)!!} \Delta^k \delta(\mathbf{r}), \quad (19)$$

which, after using ([5]): $r^2 \Delta^n \delta(\mathbf{r}) = 2n(2n+1) \Delta^{n-1} \delta(\mathbf{r})$, gives exactly Eq. (13).

As a final remark, note that all the contribution of the mean square radii is of the form $f(r)\theta(a-r)$, that is, it is different from zero only inside the sphere. One can see this writing Eq. (18) in the alternative form:

$$\phi(\mathbf{r}) = \frac{4\pi a^3 C}{3r} + 4\pi C \left(\frac{a^2}{2} - \frac{a^3}{3r} - \frac{r^2}{6} \right) \theta(a-r) \quad (20)$$

This observation is valid for any type of charge distribution and is important when we calculate the overlapping interaction energy.

3.1.2 Bravais lattice of uniformly charged spheres

We consider a Bravais lattice and, at each lattice point, a spherically charge density of the form Eq.(11). We do not impose any restriction on the sphere's radius a , so the spheres may overlap each other. The electrostatic potential at an arbitrary point \mathbf{r} of such a lattice can be written:

$$\begin{aligned}\phi(\mathbf{r}) &= \sum_{\mathbf{R}_k} \frac{\overline{r_0^0}}{|\mathbf{r} - \mathbf{R}_k|} + \sum_{\mathbf{R}_k} \sum_{n=1}^{\infty} \frac{\overline{r_0^{2n}}}{2^n n! (2n+1)!!} \Delta^n \frac{1}{|\mathbf{r} - \mathbf{R}_k|} = \\ &= 4\pi C \frac{a^3}{3} \sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} - \\ &= 2\pi C a^5 \sum_{\mathbf{R}_k} \sum_{p=0}^{\infty} \frac{a^{2p}}{2^p (p+1)! (2p+5)!!} \Delta^p \delta(\mathbf{r} - \mathbf{R}_k),\end{aligned}$$

where we have used the first relation of Eq.(7). We can further transform the above formula by using Eq.(7). One obtains:

$$\begin{aligned}\phi(\mathbf{r}) &= \frac{4\pi C a^3}{3} \sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} + 2\pi C a^5 \cdot \\ &= \sum_{\mathbf{g}} \sum_{p=0}^{\infty} \frac{(-1)^p (ag)^{2p}}{2^p (p+1)! (2p+5)!!} e^{i\mathbf{g}\mathbf{r}} = \\ &= \frac{4\pi C a^3}{3} \sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} + \frac{16\pi^2 C a^3}{\Omega} \cdot \\ &= \sum_{\mathbf{g}} \left(\frac{1}{ag^3} j_1(ag) - \frac{1}{3g^2} \right) e^{i\mathbf{g}\mathbf{r}}.\end{aligned}\tag{21}$$

At this stage, we are going to make some general remarks about the structure of the electrostatic potential, as it appears in the above equation. The first term in the r.h.s. of the above equation is the monopole contribution to the scalar potential and the second term in the r.h.s. of Eq.(21) is the contribution from all the monopole mean square radii. It is worth noting that, if we consider a Bravais lattice of neutral spheres (which means a charge density of the form: $\rho(\mathbf{r}) = C\theta(a - r) - \frac{4\pi a^3 C}{3}\delta(\mathbf{r})$), the first term of the above equation disappears. The second term is the potential inside the spheres and it is a superposition of potentials of the form $f(r - \mathbf{R}_i)\theta(a - |\mathbf{r} - \mathbf{R}_i|)$. The term which corresponds to $\mathbf{g} = 0$ is the so-called Bethe mean potential ([6]). We can see that, in fact, the mean electrostatic potential of the lattice comprises the contribution of all the infinite number of mean square radii. Only this complete potential, by Fourier transforming, will give us correct information about the real shape of the charge distribution. We can see this if we pass again to the real space taking the Fourier transform and applying the Poisson summation formula. One obtains:

$$\begin{aligned}\phi(\mathbf{r}) &= \sum_{\mathbf{R}_k} \left[\frac{4\pi C a^3}{3|\mathbf{r} - \mathbf{R}_k|} \theta(|\mathbf{r} - \mathbf{R}_k| - a) + \right. \\ &\quad \left. \frac{2\pi C}{3} (3a^2 - |\mathbf{r} - \mathbf{R}_k|^2) \theta(a - |\mathbf{r} - \mathbf{R}_k|) \right],\end{aligned}\tag{22}$$

which is exactly the superposition of the potentials of all the spheres from the lattice points. This is the expected result, as the electrostatic potential satisfies the superposition principle.

It is well-known that the series $\sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r}-\mathbf{R}_k|}$ is conditionally convergent and there exist many methods in the literature for studying it (see Refs. [1], [7] and references therein). As we are not very much interested here about what happens at infinity (surface effects), we shall consider this term as arising from the limit of a screened Coulomb potential, whose Fourier transform is well defined at the origin. Therefore, we shall write Eq.(21) in the reciprocal space as follows:

$$\begin{aligned} \phi(\mathbf{r}) = & \frac{16\pi^2 C a^3}{3} \lim_{\epsilon \rightarrow 0} \sum_{\mathbf{g}} \frac{e^{i\mathbf{g}\mathbf{r}}}{g^2 + \epsilon^2} + \frac{16\pi^2 C a^3}{\Omega} \cdot \\ & \sum_{\mathbf{g}} \left(\frac{1}{ag^3} j_1(ag) - \frac{1}{3g^2} \right) e^{i\mathbf{g}\mathbf{r}}. \end{aligned} \quad (23)$$

As the self-energy of a uniformly charged sphere is $W_s = \frac{16\pi^2 C^2 a^5}{15}$, then the electrostatic energy of the lattice is:

$$\begin{aligned} W = & \frac{32\pi^3 C^2 a^5}{3\Omega} \lim_{\epsilon \rightarrow 0} \sum_{\mathbf{g}} \frac{j_1(ag)}{g(g^2 + \epsilon^2)} + \frac{32\pi^3 C^2 a^5}{\Omega} \cdot \\ & \sum_{\mathbf{g}} \left[\frac{(j_1(ag))^2}{ag^4} - \frac{j_1(ag)}{3g^3} \right] - \frac{16\pi^2 C^2 a^5}{15} \end{aligned} \quad (24)$$

and, after we take the limit:

$$W = \frac{32\pi^3 C^2 a^4}{\Omega} \sum_{\mathbf{g}} \left[\frac{j_1(ag)}{g^2} \right]^2 - \frac{16\pi^2 C^2 a^5}{15}. \quad (25)$$

This result, which in our view is valid for arbitrary (overlapping or non-overlapping spheres), coincide with the result from Ref. [8], Eq.(41). (In our paper the structure factor $F(\mathbf{g}) = 1$, because we are considering a simple Bravais lattice). However, in Ref. [8] this result is reported as being valid only for nonoverlapping spheres and is subsequently corrected for overlap by adding a sum in the direct space. This discrepancy can be explained as follows: the first term in the r.h.s. of Eq.(24) is the long-range interaction energy, while the second is the overlapping energy. The second term is therefore zero in the case of nonoverlapping spheres. It follows that, for zero overlap we have:

$$\sum_{\mathbf{g}} \frac{(j_1(ag))^2}{ag^4} = \sum_{\mathbf{g}} \frac{j_1(ag)}{3g^3} \quad (26)$$

and the interaction energy can be written in two equivalent forms:

$$\begin{aligned} W = & \frac{32\pi^3 C^2 a^5}{3\Omega} \sum_{\mathbf{g}} \frac{j_1(ag)}{g^3} - \frac{16\pi^2 C^2 a^5}{15} = \\ & \frac{32\pi^3 C^2 a^4}{\Omega} \sum_{\mathbf{g}} \frac{(j_1(ag))^2}{g^4} - \frac{16\pi^2 C^2 a^5}{15}. \end{aligned}$$

Evidently, the model of overlapping spheres having uniform charge densities is counterintuitive, but our method of calculation can be applied for arbitrary charge densities, as we shall do in the next sections.

It is worth analyzing in more detail our Eq. (24) and comparing our method with that of Ref. [8]. The method of charge spreading introduced in Ref.[8] is based on a theorem of electrostatics which asserts that the electrostatic energy of two point charges coincide with the electrostatic energy of two spherically symmetric extended charges. If we look at our Eq.(24), we see that this means to admit that the term $\lim_{\epsilon \rightarrow 0} \sum_{\mathbf{g}} \frac{j_1(ag)}{g(g^2+\epsilon^2)}$ exactly cancel the term $\sum_{\mathbf{g}} \frac{j_1(ag)}{3g^3}$. This does not mean that we have solved on this occasion the problem of summing the conditionally Coulomb series but that using such a mathematical machinery we get widely accepted physical results. Having in mind this conclusion, we shall apply the same formalism in the next sections, for other interesting charge densities.

3.2 Other charge distributions

3.2.1 Gaussian charge distribution

We consider now that the charge density has a gaussian form : $\rho(\mathbf{r}) = Ce^{-\lambda r^2}$, where C and λ are adjustable parameters. Then, the charge mean square radii of order n has the form:

$$\overline{r_0^{2n}} = \frac{2\pi C}{\lambda^{n+\frac{3}{2}}} \Gamma(n + \frac{3}{2}), \quad (27)$$

where Γ is the Gamma function ([9]). From Eq. (1) we obtain in this case:

$$e^{-\lambda r^2} = \pi^{3/2} \sum_{n=0}^{\infty} \frac{1}{2^{2n} n! \lambda^{n+\frac{3}{2}}} \Delta^n \delta(\mathbf{r}), \quad (28)$$

which, after Fourier transformation becomes the Taylor expansion of the exponential function:

$$e^{-\frac{k^2}{4\lambda}} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{k^2}{4\lambda} \right)^n. \quad (29)$$

Then, for the electrostatic potential produced by all the ions at the point \mathbf{r} one obtains:

$$\begin{aligned} \phi(\mathbf{r}) = & \frac{\pi^{3/2} C}{\lambda^{3/2}} \sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} + \frac{4\pi^{5/2} C}{\Omega \lambda^{3/2}} \cdot \\ & \sum_{\mathbf{g}} \frac{1}{g^2} (e^{-\frac{g^2}{4\lambda}} - 1) e^{i\mathbf{g}\mathbf{r}}, \end{aligned} \quad (30)$$

or, as a single sum in the reciprocal space:

$$\begin{aligned} \phi(\mathbf{r}) = & \frac{4\pi^{5/2} C}{\Omega \lambda^{3/2}} \lim_{\epsilon \rightarrow 0} \sum_{\mathbf{g}} \frac{e^{i\mathbf{g}\mathbf{r}}}{g^2 + \epsilon^2} + \frac{4\pi^{5/2} C}{\Omega \lambda^{3/2}} \cdot \\ & \sum_{\mathbf{g}} \frac{1}{g^2} (e^{-\frac{g^2}{4\lambda}} - 1) e^{i\mathbf{g}\mathbf{r}}. \end{aligned} \quad (31)$$

Taking the Fourier transform and using the Poisson summation formula, we obtain from the above equation:

$$\begin{aligned}\phi(\mathbf{r}) &= \frac{\pi^{3/2}C}{\Omega\lambda^{3/2}} \sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} + \frac{\pi^{3/2}C}{\Omega\lambda^{3/2}} \cdot \\ &\quad \sum_{\mathbf{R}_k} \left(\frac{\text{erf}(\sqrt{\lambda}|\mathbf{r} - \mathbf{R}_k|)}{|\mathbf{r} - \mathbf{R}_k|} - \frac{1}{|\mathbf{r} - \mathbf{R}_k|} \right) \\ &= \frac{\pi^{3/2}C}{\Omega\lambda^{3/2}} \sum_{\mathbf{R}_k} \frac{\text{erf}(\sqrt{\lambda}|\mathbf{r} - \mathbf{R}_k|)}{|\mathbf{r} - \mathbf{R}_k|},\end{aligned}$$

which is exactly the linear superposition of the electrostatic potentials of all the gaussian charge distributions of the lattice.

We compare again our view with that of Ref.[8] (Eqs.(51)-(53)) and we note that, as in this case the charge distributions are infinite, they overlap in all the space. That is why the contribution of the mean square radii can be interpreted in this case as an "overlap correction", if we are interested in studying a lattice of point charge. Note that, if the charge density is finite, the electrostatic potential of all the mean square radii is different from zero only inside the source, while for infinite charge distributions (but rapidly decreasing at infinity), the potential of the mean square radii is significantly different from zero only in the region where the charge distribution is significantly different from zero. We have obtained in the above equation that, for a charge distribution of the form $\rho(\mathbf{r}) = Ce^{-\lambda r^2}$, the potential of its mean square radii is proportional to $\frac{\text{erfc}(\sqrt{\lambda}r)}{r}$.

The self-energy of a gaussian charge distribution is $W_s = \frac{\pi^{5/2}C^2}{\lambda^{5/2}2^{1/2}}$ and the electrostatic energy of the lattice:

$$W = \frac{2\pi^4C}{\omega\lambda^3} \sum_{\mathbf{g}} \frac{1}{g^2} e^{-\frac{g^2}{2\lambda}} - \frac{\pi^{5/2}C^2}{\lambda^{5/2}2^{1/2}}.$$

3.2.2 Exponential charge distribution

We consider now an exponential charge density of the form: $\rho(\mathbf{r}) = Ce^{-\lambda r}$, where C and $\lambda > 0$ are adjustable parameters. A charge mean square radius of order n has the expression:

$$\overline{r_0^{2n}} = \frac{4\pi C}{\lambda^{2n+3}} \Gamma(2n+3). \quad (32)$$

Eq. (1) becomes in this case:

$$e^{-\lambda r} = 8\pi \sum_{n=0}^{\infty} \frac{n+1}{\lambda^{2n+3}} \Delta^n \delta(\mathbf{r}) \quad (33)$$

and, after taking the Fourier transform, we find the usual Taylor expansion:

$$\frac{1}{\left(1 + \frac{k^2}{\lambda^2}\right)^2} = \sum_{n=0}^{\infty} (-1)^n (n+1) \left(\frac{k^2}{\lambda^2}\right)^n. \quad (34)$$

The electrostatic potential produced by such a lattice at an arbitrary point \mathbf{r} is:

$$\begin{aligned}\phi(\mathbf{r}) = & \frac{8\pi C}{\lambda^3} \sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} + \frac{32\pi^2 C}{\Omega \lambda^3} \cdot \\ & \sum_{\mathbf{g}} \frac{1}{g^2} \left[\frac{\lambda^4}{(\lambda^2 + g^2)^2} - 1 \right] e^{i\mathbf{g}\mathbf{r}},\end{aligned}\quad (35)$$

or, as a single sum in the reciprocal space,

$$\phi(\mathbf{r}) = \frac{32\pi^2 C}{\lambda^3 \Omega} \sum_{\mathbf{g}} \frac{1}{g^2} \frac{\lambda^4}{(\lambda^2 + g^2)^2} e^{i\mathbf{g}\mathbf{r}}. \quad (36)$$

The self-energy of such a charge distribution is $W_s = \frac{10\pi^2 C^2}{\lambda^5}$ and the electrostatic energy of the lattice is:

$$W = \frac{128\pi^3 \lambda^2 C^2}{\Omega} \sum_{\mathbf{g}} \frac{1}{g^2 (\lambda^2 + g^2)^4} - \frac{10\pi^2 C^2}{\lambda^5}. \quad (37)$$

3.2.3 Slater-type charge distribution without angular dependence

In Ref. [10] Slater proposed a radial wave function appropriate for many-electron atoms and ions of the form:

$$\psi(r) = r^{n^*-1} e^{-\frac{Z-s}{n^*} r},$$

where n^* is an effective quantum number, Z is the atomic number and s a screening constant. We consider now that at each node of our Bravais lattice there is a charge density which corresponds to Slater's radial wave function:

$$\rho(r) = C r^{2(n^*-1)} e^{-2\lambda r}, \quad (38)$$

where $\lambda \equiv \frac{Z-s}{n^*}$ and C is a constant. The mean square charge radii of order p which corresponds to such a charge density is:

$$\overline{r_0^{2p}} = \frac{4\pi C (2p + 2n^*)!}{(2\lambda)^{2p+2n^*+1}}.$$

Eq.(1) becomes in this case:

$$r^{2(n^*-1)} e^{-2\lambda r} = 4\pi \sum_{p=0}^{\infty} \frac{(2p + 2n^*)!}{2^p p! (2p + 1)!! (2\lambda)^{2p+2n^*+1}} \Delta^p \delta(\mathbf{r}) \quad (39)$$

and, after taking the Fourier transform:

$$\begin{aligned}\Gamma(2n^* + 1) {}_2F_1 \left(\frac{2n^* + 1}{2}, n^* + 1; \frac{3}{2}; -\frac{k^2}{4\lambda^2} \right) = \\ \sum_{p=0}^{\infty} \frac{(2p + 2n^*)! (-1)^p k^{2p}}{2^p p! (2p + 1)!! (2\lambda)^{2p}},\end{aligned}$$

which is exactly the defining series of the Gauss hypergeometric function. The electrostatic potential at an arbitrary point of such a lattice is:

$$\phi(\mathbf{r}) = \frac{4\pi C(2n^*)!}{(2\lambda)^{2n^*+1}} \sum_{\mathbf{R}_k} \frac{1}{|\mathbf{r} - \mathbf{R}_k|} + \frac{16\pi^2 C(2n^*)!}{\Omega(2\lambda)^{2n^*+1}} \cdot \sum_{\mathbf{g}} \frac{1}{g^2} \left\{ \frac{i\lambda}{2n^*g} \left[\left(\frac{2\lambda}{2\lambda + ig} \right)^{2n^*} - \left(\frac{2\lambda}{2\lambda - ig} \right)^{2n^*} \right] - 1 \right\} e^{i\mathbf{g}\mathbf{r}},$$

or, as a single sum in the reciprocal space:

$$\phi(\mathbf{r}) = \frac{16\pi^2 C(2n^*)!}{\Omega(2\lambda)^{2n^*+1}} \cdot \sum_{\mathbf{g}} \frac{i\lambda}{2n^*g^3} \left[\left(\frac{2\lambda}{2\lambda + ig} \right)^{2n^*} - \left(\frac{2\lambda}{2\lambda - ig} \right)^{2n^*} \right] e^{i\mathbf{g}\mathbf{r}}. \quad (40)$$

The self-energy of such a charge distribution is:

$$W_s = \frac{\pi^2 C^2 \Gamma(2n^*)}{2^{4n^*-1} \lambda^{4n^*+1}} \left[4n^* \Gamma(2n^*) - \frac{2}{\sqrt{\pi}} \Gamma\left(2n^* + \frac{1}{2}\right) \right] \quad (41)$$

and the electrostatic energy of the lattice is:

$$W = \frac{16\pi^3 i C^2 [\Gamma(2n^*)]^2}{\Omega} \cdot \sum_{\mathbf{g}} \frac{[(2\lambda - ig)^{2n^*} - (2\lambda + ig)^{2n^*}]}{g^4 (4\lambda^2 + g^2)^{3n^*}} \sin \left[2n^* \arctan \frac{g}{2\lambda} \right] - \frac{\pi^2 C^2 \Gamma(2n^*)}{2^{4n^*-1} \lambda^{4n^*+1}} \left[4n^* \Gamma(2n^*) - \frac{2}{\sqrt{\pi}} \Gamma\left(2n^* + \frac{1}{2}\right) \right].$$

4 Conclusions

We have written the electrostatic potential and the electrostatic interaction energy in a Bravais lattice of arbitrary charge distributions as sums in the reciprocal space. We have shown that the so-called overlapping correction, which have been written in Ref. [8] as a sum in the direct space, is in fact the contribution of the mean square radii to the interaction energy.

We have considered in this paper only charge densities with spherical symmetry. In the case of charge distributions which have angular dependence do not appear important technical complications and in many cases the results are finite linear combinations of the results above obtained, with some weights given by the values of the angular integrals. For example, if we consider a Slater-type charge distribution of the type $\rho(\mathbf{r}) = C r^{2(n^*-1)} e^{-2\lambda r} |Y_{1m}(\theta, \phi)|^2$, where Y_{1m} , $m = 0, \pm 1$ is a spherical harmonic ([9]), the only non-zero multipoles are the monopole and the quadrupole together with their infinite number of mean square radii. Therefore, after we have found the weights of these two type of multipoles, the calculation follows as in Sec. 2.3.3 and the final result can be written as a linear superposition. Such elaborate calculations will be the subject of an other paper.

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